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(54) Title: **SILICONE POLYETHER BLOCK COPOLYMERS**

(57) Abstract: (AB)_n silicone polyethers that are polyorganosiloxane-polyoxethylen block copolymers having the average formula, $[-R^1(R_2SiO)_x(R_2SiR^1O)(C_2H_4O)_y]_z-$, where x and y are greater than 4, and x/(x+y) ranges from 0.2 to 0.9, z is greater than 2, R is independently a monovalent organic group, and R¹ is a divalent organic group containing 2 to 12 carbons are disclosed. Such (AB)_n silicone polyethers are useful to prepare vesicle compositions and stable aqueous dispersions which can be used to entrap, and subsequently deliver after application, a personal, household care, or health care ingredient.



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SILICONE POLYETHER BLOCK COPOLYMERS

Description

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CROSS REFERENCE TO RELATED APPLICATIONS

[0001] This application claims priority to US Patent Application No. 60/563,663 filed April 20, 2004 and US Patent Application No. 60/611,229 filed September 17, 2004.

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FIELD OF THE INVENTION

[0002] The present invention relates to $(AB)_n$ silicone polyethers that are polyorganosiloxane-polyoxyethylene block copolymers having the average formula



where x and y are greater than 4, and $x/(x+y)$ ranges from 0.2 to 0.9, z is greater than 2,

15

R is independently a monovalent organic group, and R^1 is a divalent organic group containing 2 to 30 carbons. The $(AB)_n$ silicone polyethers of the present invention can be used to prepare vesicle compositions and stable aqueous dispersions which can be used to entrap, and subsequently deliver after application, a personal, household care, or health care ingredient.

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BACKGROUND OF THE INVENTION

[0003] Silicone surfactants have been designed for various applications by combining a hydrophobic organopolysiloxane with various hydrophilic moieties. For example, the silicone surfactants known as silicone polyethers (SPEs) are based on copolymer structures of polyorganosiloxanes having pendant polyoxyalkylene groups. Most commonly, the copolymer structures of silicone polyethers are the "rake" type, where a predominately linear polyorganosiloxane provides the "backbone" of the copolymer architecture with pendant polyoxyalkylene groups forming the "rake". "ABA" structures are also common, where a pendant polyoxyalkylene group is at each molecular terminal of a linear polyorganosiloxane. $(AB)_n$ silicone polyethers are also known, wherein blocks of a siloxane units and polyether units repeat to form the copolymer. $(AB)_n$ SPEs are not as predominant in the art as the rake or ABA silicone polyethers. For example, there are numerous teachings describing various

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ake and ABA silicone polyethers structures for applications in many personal, household, and health care compositions as emulsifiers, wetting agents, and general-purpose aqueous surfactants. More recently, the aggregation behavior of rake and ABA silicone polyethers has been reported.

5 [0004] Long-standing needs in the field of cosmetic and drug formulation/delivery field are to identify vesicle compositions that form and entrap actives easily, are stable under various chemical and mechanical stresses, and yet are able to deliver the actives in a controlled manner under desired conditions. Vesicles derived from silicone surfactants, and more particularly silicone polyether surfactants, are of interest because of additional inherent
10 benefits that this class of surfactants possesses vs. other types. For example, silicone polyether surfactants often have improved aesthetics in personal care formulations.

[0005] US Patents 5,364,633 and 5,411,744 by Hill teaches the self-assembly of silicone vesicles in aqueous dispersions of certain silicone polyethers. PCT application US03/38455 by Lin teaches the entrapment of various oils in silicone vesicles and their use in various
15 personal care formulations.

[0006] The present inventors have discovered that certain $(AB)_n$ silicone polyethers form unique dispersions in aqueous media. In one embodiment, certain defined $(AB)_n$ SPE structures will form vesicle compositions in aqueous media. In a second embodiment, certain $(AB)_n$ SPE structures form stable dispersions that can be used to create emulsions. These
20 stable dispersions and vesicles can be used to formulate compositions for the delivery of pharmaceutical and personal care actives.

[0007] While $(AB)_n$ silicone polyether block copolymers are known, the selection of the specific structures or certain molecular variables that enables the copolymers to form stable dispersions in aqueous media is heretofore unknown.

25 [0008] U.S. Patents Nos. 3,957,842 and 4,022,941 by Prokai et al. teach linear siloxane-polyoxyalkylene $(AB)_n$ block copolymers having an average molecular weight of at least about 30,000. The '842 and '941 patents further teach the use of the linear siloxane-polyoxyalkylene $(AB)_n$ block copolymers in polyurethane forming compositions, as well as the cured foams and articles produced therefrom.

30 [0009] U.S. Patent Nos. 5,472,686 and 5,660,819 by Tsubaki et al. teach cosmetic formulations containing a linear polysiloxane-polyoxyalkylene block copolymer as the main

component. However, the '686 and '819 patents do not teach polysiloxane-polyoxyalkylene block copolymers structures to form vesicles.

[0010] U.S. Patent 5,767,219 teaches a polysiloxane-polyether block copolymer having excellent heat resistance, which is characterized by the molecular structure consisting of repetition of diorganopolysiloxane units and polyoxyalkylene units having a bisphenol linkage of the formula $-\text{O}-\text{Pn}-\text{CMe}_2-\text{Pn}-\text{O}-$ in the unit, Pn being a 1,4-phenylene group and Me is a methyl group. The '219 patent does not teach polysiloxane-polyoxyalkylene block copolymers structures to form vesicles.

[0011] The present inventors have discovered not all of the $(\text{AB})_n$ silicone polyethers structures as broadly taught in the art will form stable aqueous dispersions, and in particular aqueous vesicular structures. Rather, the inventors have discovered that it is essential for the $(\text{AB})_n$ silicone polyethers to have certain molecular characteristics in order to form stable aqueous dispersions and vesicles.

15 SUMMARY OF THE INVENTION

[0012] The $(\text{AB})_n$ silicone polyethers of the present invention are polyorganosiloxane-polyoxyethylene block copolymers having the average formula (*Formula I*);



where x and y are greater than 4, $x/(x+y)$ ranges from 0.2 to 0.9,

z is greater than 2,

R is independently a monovalent organic group, and

R^1 is a divalent organic group containing 2 to 30 carbons.

[0013] In a first embodiment of the present invention, the $(\text{AB})_n$ SPEs of Formula I have a value of x (i.e. the degree of polymerization, DP, of the polysiloxane chain in the siloxane units) that ranges from 20 to 100, alternatively from 30 to 75. These structures form vesicles in aqueous media.

[0014] In a second embodiment of the present invention, the $(\text{AB})_n$ SPEs of Formula I have a value of x (i.e. the degree of polymerization, DP, of the polysiloxane chain in the siloxane units) that ranges from 5 to 19, alternatively from 5 to 15. These structures form stable dispersions in aqueous media having a particle size of less than 10 micrometers.

[0015] The present invention further provides a process to prepare polyorganosiloxane-polyoxyethylene block copolymers comprising reacting;

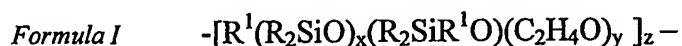
- a) a SiH terminated organopolysiloxane,
- b) a polyoxyethylene having an unsaturated hydrocarbon group at each molecular terminal,
- c) a hydrosilylation catalyst,
- d) optionally a solvent,
- e) optionally an organic endblocker compound having a mono-terminally unsaturated hydrocarbon group,

wherein the mole ratio of the unsaturated hydrocarbon groups to SiH in the reaction is at least 1:1.

[0016] The vesicle compositions and stable aqueous dispersions prepared from the (AB)_n SPEs of the present invention can be used to entrap, and subsequently deliver after application, a personal, household care, or health care ingredient.

DETAILED DESCRIPTION OF THE INVENTION

[0017] The present invention provides a polyorganosiloxane-polyoxyethylene block copolymer having the average formula;



where

x and y are greater than 4, and x/(x+y) ranges from 0.2 to 0.9,

z is greater than 2,

R is independently a monovalent organic group,

R¹ is a divalent organic group containing 2 to 30 carbons.

[0018] The siloxane block in Formula I is a predominately linear siloxane polymer having the formula (R₂SiO)_x, wherein R is independently selected from a monovalent organic group, x is an integer greater than 4. In a first embodiment the value of x (i.e. the degree of polymerization, DP, of the polysiloxane chain ranges from 20 to 100, alternatively from 30 to 75. These structures form vesicles in aqueous media, as discussed supra. In a second

embodiment, the value of x ranges from 5 to 19, alternatively from 5 to 15. These structures form stable dispersions in aqueous media having a particle size of less than 10 micrometers, also discussed supra.

[0019] The organic groups represented by R in the siloxane polymer are free of aliphatic unsaturation. These organic groups may be independently selected from monovalent hydrocarbon and monovalent halogenated hydrocarbon groups free of aliphatic unsaturation. These monovalent groups may have from 1 to 20 carbon atoms, alternatively 1 to 10 carbon atoms, and are exemplified by, but not limited to alkyl groups such as methyl, ethyl, propyl, butyl, pentyl, hexyl, heptyl, octyl, undecyl, and octadecyl; cycloalkyl such as cyclohexyl; aryl such as phenyl, tolyl, xylyl, benzyl, and 2-phenylethyl; and halogenated hydrocarbon groups such as 3,3,3-trifluoropropyl, 3-chloropropyl, and dichlorophenyl. At least 50 percent, alternatively at least 80%, of the organic groups free of aliphatic unsaturation in the organopolysiloxane may be methyl (denoted as Me). Typically, the siloxane block is a predominately linear polydimethylsiloxane having the formula $(\text{Me}_2\text{SiO})_x$, where x is as defined above.

[0020] The polyoxyethylene block of the silicone polyether is represented by the formula $(\text{C}_2\text{H}_4\text{O})_y$, wherein y is greater than 4, alternatively y can range from 5 to 45, or alternatively from 5 to 25.

[0021] At least one end of each polyoxyalkylene block in Formula I is linked to a siloxane block by a divalent organic group, designated R^1 . This linkage is determined by the reaction employed to prepare the $(\text{AB})_n$ block silicone polyether copolymer. The divalent organic groups of R^1 may be independently selected from divalent hydrocarbons containing 2 to 30 carbons and divalent organofunctional hydrocarbons containing 2 to 30 carbons. Representative, non-limiting examples of such divalent hydrocarbon groups include;

ethylene, propylene, butylene, pentylene, hexylene, heptylene, octylene, and the like.

Representative, non-limiting examples of such divalent organofunctional hydrocarbons groups include acrylate and methacrylate. Typically, R^1 is propylene, $(-\text{CH}_2\text{CH}_2\text{CH}_2-)$.

[0022] The $(\text{AB})_n$ block silicone polyethers are endblocked. The endblocking unit is also determined by the reaction employed to prepare the $(\text{AB})_n$ block silicone polyether copolymer, which is generally the residual reactive groups of the reactants used. For example, the $(\text{AB})_n$ block silicone polyether copolymers can be prepared by the metal

catalyzed hydrosilylation reaction of a diallyl polyether (i.e. an allyl group is present on each molecular terminal end) with a SiH terminated polyorganosiloxane. The resulting (AB)_n block silicone polyether copolymer would have polyoxyalkylene blocks linked to the silicone blocks via a propyleneoxy group (-CH₂CH₂CH₂O-), and using a slight molar excess of the allyl polyether would result in an allyl endblock unit (-CH₂CHCH₂). Alternative endblock units can result from the addition of other molecules in the reaction employed to prepare the (AB)_n block silicone polyether copolymer that are capable of reacting with the siloxane or polyether block intermediates. For example, the addition of organic compounds having mono-terminated aliphatic unsaturation (such as a mono allyl terminated polyether) will result in the endcapping of the (AB)_n block silicone polyether copolymer with that organic compound. Preferably, the endblocking units of the (AB)_n block silicone polyether is an allyl ether (CH₂=CHCH₂O-) or allyl polyether.

[0023] The molecular weights of the (AB)_n block silicone polyether copolymers will be determined by the number of repeating siloxane and polyoxyethylene blocks, as indicated by the subscript z in Formula I. Typically, the value of z is such to provide weight average molecular weights (M_w) to range from 1,500 to 150,000, alternatively, from 10,000 to 100,000.

[0024] In order to form vesicles or stable aqueous dispersions, the (AB)_n SPEs of the present invention have a molar ratio of the total siloxane units to the polyoxyethylene units in the (AB)_n block silicone polyether. This molecular parameter is expressed by the value of x/(x+y) in Formula I. The value of x/(x+y) can vary from 0.2 to 0.9, or alternatively from 0.4 to 0.9.

[0025] The (AB)_n SPEs of the present invention can be prepared by any method known in the art for preparing such block copolymers. Alternatively, the (AB)_n SPEs of the present invention are prepared according the methods described infra.

[0026] The present invention further provides a process to prepare polyorganosiloxane-polyoxyethylene block copolymers comprising reacting;

- a) a SiH terminated organopolysiloxane,
- b) a polyoxyethylene having an unsaturated hydrocarbon group at each molecular terminal,
- c) a hydrosilylation catalyst,
- d) optionally a solvent,

e) optionally an organic endblocker compound having a mono-terminally unsaturated hydrocarbon group,

wherein the mole ratio of the unsaturated organic groups to SiH in the reaction is at least 1:1.

[0027] The SiH terminated organopolysiloxanes useful in the process of the present invention

5 can be represented by the formula $M'DM'$, where "M'" means a siloxane unit of formula $R_2HSiO_{1/2}$, "D" means a siloxane unit of formula $R_2SiO_{2/2}$, where R is independently a monovalent organic group as defined above. Typically, the SiH terminated organopolysiloxane is a dimethylhydrogensiloxy-terminated polydimethylsiloxane having the average formula $Me_2HSiO(Me_2SiO)_xSiHMe_2$, where x is as defined above. SiH terminated

10 organopolysiloxanes and methods for their preparation are well known in the art.

[0028] The polyoxyethylene useful in the process of the present invention can be any polyoxyethylene comprising the average formula $-(C_2H_4O)_y-$, where y is defined as above, and is terminated at each molecular chain end (i.e. alpha and omega positions) with a unsaturated organic group. The unsaturated organic group can be an unsaturated

15 hydrocarbon group such as alkenyl or alkynyl group. Representative, non-limiting examples of the alkenyl groups are shown by the following structures; $H_2C=CH-$, $H_2C=CHCH_2-$, $H_2C=C(CH_3)CH_2-$, $H_2C=CHCH_2CH_2-$, $H_2C=CHCH_2CH_2CH_2-$, and $H_2C=CHCH_2CH_2CH_2CH_2-$. Representative, non-limiting examples of alkynyl groups are shown by the following structures; $HC\equiv C-$, $HC\equiv CCH_2-$, $HC\equiv CC(CH_3)-$, $HC\equiv CC(CH_3)_2-$,

20 $HC\equiv CC(CH_3)_2CH_2-$. Polyoxyethylenes having an unsaturated hydrocarbon group at each molecular terminal are known in the art, and many are commercially available. Alternatively, the unsaturated organic group can be an organofunctional hydrocarbon such as an acrylate, methacrylate and the like. Typically the polyoxyethylene has the average formula $H_2C=CHCH_2O(CH_2CH_2O)_yCH_2CH=CH_2$ wherein y is greater than 4, or alternatively ranges from range from 5 to 30, or alternatively from 5 to 22.

25 [0029] The SiH terminated organopolysiloxane and polyoxyethylene having an unsaturated organic group at each molecular terminal are reacted in the presence of a hydrosilylation catalyst, which are known in the art. Such hydrosilylation catalysts are illustrated by any metal-containing catalyst which facilitates the reaction of silicon-bonded hydrogen atoms of

30 the SiH terminated organopolysiloxane with the unsaturated hydrocarbon group on the

polyoxyethylene. The metals are illustrated by ruthenium, rhodium, palladium, osmium, iridium, or platinum.

[0030] Hydrosilylation catalysts are illustrated by the following; chloroplatinic acid, alcohol modified chloroplatinic acids, olefin complexes of chloroplatinic acid, complexes of
5 chloroplatinic acid and divinyltetramethyldisiloxane, fine platinum particles adsorbed on carbon carriers, platinum supported on metal oxide carriers such as $\text{Pt}(\text{Al}_2\text{O}_3)$, platinum black, platinum acetylacetonate, platinum(divinyltetramethyldisiloxane), platinous halides exemplified by PtCl_2 , PtCl_4 , $\text{Pt}(\text{CN})_2$, complexes of platinous halides with unsaturated compounds exemplified by ethylene, propylene, and organovinylsiloxanes, styrene
10 hexamethyldiplatinum, and $\text{RhCl}_3(\text{Bu}_2\text{S})_3$.

[0031] The amount of hydrosilylation catalyst that is used is not narrowly limited as long as there is a sufficient amount to accelerate a reaction between the polyoxyethylene having an unsaturated hydrocarbon group at each molecular terminal and the SiH terminated organopolysiloxane at room temperature or at temperatures above room temperature. The
15 exact necessary amount of this catalyst will depend on the particular catalyst utilized and is not easily predictable. However, for platinum-containing catalysts the amount can be as low as one weight part of platinum for every one million weight parts of components the polyoxyethylene having an unsaturated hydrocarbon group at each molecular terminal and the SiH terminated organopolysiloxane. The catalyst can be added at an amount 10 to 120
20 weight parts per one million parts of components the polyoxyethylene having an unsaturated organic group at each molecular terminal and the SiH terminated organopolysiloxane, but is typically added in an amount from 10 to 60 weight parts per one million parts of the polyoxyethylene having an unsaturated organic group at each molecular terminal and the SiH terminated organopolysiloxane.

[0032] The hydrosilylation reaction can be conducted neat or in the presence of d), a solvent. The solvent can be an alcohol such as methanol, ethanol, isopropanol, butanol, or n-propanol, a ketone such as acetone, methylethyl ketone, or methyl isobutyl ketone; an aromatic hydrocarbon such as benzene, toluene, or xylene; an aliphatic hydrocarbon such as heptane, hexane, or octane; a glycol ether such as propylene glycol methyl ether, dipropylene glycol
30 methyl ether, propylene glycol n-butyl ether, propylene glycol n-propyl ether, or ethylene glycol n-butyl ether, a halogenated hydrocarbon such as dichloromethane, 1,1,1-

trichloroethane or methylene chloride, chloroform, dimethyl sulfoxide, dimethyl formamide, acetonitrile, tetrahydrofuran, white spirits, mineral spirits, or naphtha.

[0033] The amount of solvent can be up to 50 weight percent, but is typically from 20 to 50 weight percent, said weight percent being based on the total weight of components in the

5 hydrosilylation reaction. The solvent used during the hydrosilylation reaction can be subsequently removed from the resulting silicone polyether by various known methods.

[0034] Optional component e) is an organic endblocker compound having a mono-terminally unsaturated organic group. The addition of this component can be used to adjust the molecular weight of the block silicone polyether. Typically, these are chosen from

10 polyoxyethylenes comprising the average formula $-(C_2H_4O)_y-$, where y is defined as above, and is terminated at one molecular chain end with an unsaturated group, such as an alkenyl or alkynyl group.

[0035] Additional components can be added to the hydrosilylation reaction which are known to enhance such reactions. These components include salts such as sodium acetate which

15 have a buffering effect in combination with platinum catalysts.

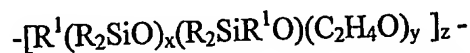
[0036] In a first embodiment of the present invention, the $(AB)_n$ SPEs of Formula I have a value of x (i.e. the degree of polymerization, DP, of the polysiloxane chain in the siloxane units) that ranges from 20 to 100, alternatively from 30 to 75. These structures form vesicles in aqueous media. Such vesicle compositions can be prepared by mixing the $(AB)_n$ SPEs

20 with water using any technique known common in the state of the art for creating vesicle compositions. The type and extent of the mixing technique will depend on the specific structure of the $(AB)_n$ SPE chosen. For example, some $(AB)_n$ SPEs will form vesicle compositions spontaneously when mixed with water, while others $(AB)_n$ SPEs will require the presence of a water soluble solvent to facilitate the formation of vesicles.

25 [0037] Typically, the vesicle compositions are prepared using a process comprising;

I) combining,

A) a $(AB)_n$ silicone polyether copolymer having the average formula;



where x and y are greater than 4, and $x/(x+y)$ ranges from 0.2 to 0.9,

z is greater than 2,

R is independently a monovalent organic group, and

R^1 is a divalent organic group containing 2 to 30 carbons.

B) optionally, a water miscible volatile solvent,

C) water,

to form an aqueous dispersion of the $(AB)_n$ silicone polyether copolymer,

5 II) optionally, removing the water miscible volatile solvent from the aqueous dispersion to form the vesicle composition.

[0038] The $(AB)_n$ SPEs, component A), is the same as described above. Optional component B) is a water-miscible volatile solvent. As used herein "water-miscible" means the solvent forms a dispersion with water at room temperature for at least several hours. "Volatile" means the solvent has a higher vapor pressure than water at various temperatures. As such, when the aqueous dispersion of the organopolysiloxane and solvent are subjected to conditions to remove the solvent, such as heating the dispersion under reduced pressures, the solvent is primarily removed first, allowing all or most of the water to remain in the composition.

15 [0039] Suitable water-miscible volatile solvents for vesicle dispersion preparation include organic solvents such as alcohols, ethers, glycols, esters, acids, halogenated hydrocarbons, diols. The organic solvents should be miscible with water at the proportion and lower in order to effectively disperse silicones and maintain stable and uniform dispersion overtime. For the purpose of illustration, water-miscible alcohols include methanol, ethanol, propanol, isopropanol, butanol, and higher hydrocarbon alcohols; ethers include glycol ethers, methyl-ethyl ether, methyl isobutyl ether (MIBK), etc; glycols include propylene glycols, esters include esters of triglycerol, the esterification products of acid and alcohol; halogenated hydrocarbons include chloroform. Typically water-miscible organic solvents are solvents with relatively low boiling points ($<100^\circ\text{C}$) or high evaporation rate, so they may be removed under vacuum with ease. The most preferred water-miscible organic solvents for this invention are volatile alcohols including methanol, ethanol, isopropanol, and propanol. These alcohols can be removed from aqueous mixtures containing silicone vesicle dispersions via vacuum stripping at ambient temperature.

25 [0040] The order of mixing components A), B), and C) is not critical, but typically A) and B) are first mixed and then water added to the mixture. There are no special requirements or

conditions needed for effecting the mixing of components A), B), and C). The mixing can be conducted in a batch, semi-continuous, or continuous process.

[0041] The amount of components A), B), and C) can vary in the process, but typically range as follows;

- 5 A) 2 to 50 wt%, alternatively 2 to 25 wt %, or alternatively 2 to 15 wt%,
- B) 0 to 50 wt%, alternatively 2 to 25 wt %, or alternatively 2 to 15 wt%,
- C) sufficient amount to provide the sum of the wt% of A), B), and C) to equal 100%

[0042] The amount of B) water-miscible volatile solvent used to disperse the (AB)_n SPEs depends on the type of organopolysiloxane and how much hydrophilic groups are present.

- 10 Typically, the aqueous mixture to effectively disperse silicones comprises of 5 to 80 parts of solvent and 20 to 95 parts of water; alternatively 5 to 50 parts of water, or alternatively 10 to 40 parts water.

[0043] In a second embodiment of the present invention, the (AB)_n SPEs of Formula I have a value of x (i.e. the degree of polymerization, DP, of the polysiloxane chain in the siloxane units) that ranges from 5 to 19, alternatively from 5 to 10. These structures form stable
15 dispersions in aqueous media having a particle size of less than 10 micrometers. The stable aqueous dispersions are prepared by mixing the (AB)_n SPEs of the second embodiment with water. The mixing technique is not critical, as the (AB)_n SPEs of the second embodiment easily form stable dispersions from simply mixing the SPEs as defined with water.

- 20 [0044] The vesicle compositions and stable aqueous dispersions prepared from the (AB)_n SPEs of the present invention can be used to entrap, and subsequently deliver after application, a personal, household care, or health care ingredient. A listing of possible personal, household, or health care ingredients is taught in WO 03/101412, which is incorporated herein by reference. The personal or health care ingredient can also be selected
25 from a personal or health care "active", that is, any compound known to have either cosmetic and/or pharmaceutical activity. A representative listing of such personal or health care actives are disclosed in US Patent 6,168,782, which is hereby incorporated by reference.

[0045] Compositions prepared according to the invention can be used in various over-the-counter (OTC) personal care compositions, health care compositions, and household care
30 compositions, but especially in the personal care arena. Thus, they can be used in antiperspirants, deodorants, skin creams, skin care lotions, moisturizers, facial treatments

such as acne or wrinkle removers, personal and facial cleansers, bath oils, perfumes, colognes, sachets, sunscreens, pre-shave and after-shave lotions, liquid soaps, shaving soaps, shaving lathers, hair shampoos, hair conditioners, hair sprays, mousses, permanents, depilatories, hair cuticle coats, make-ups, color cosmetics, foundations, blushes, lipsticks, lip

5 balms, eyeliners, mascaras, oil removers, color cosmetic removers, nail polishes, and powders.

EXAMPLES

[0046] The following examples are presented to further illustrate the compositions and methods of this invention, but are not to be construed as limiting the invention. All parts and percentages in the examples are on a weight basis and all measurements were obtained at about 23°C, unless indicated to the contrary.

[0047] Representative $(AB)_n$ silicone polyethers, herein designated as $(AB)_n$ SPEs, were prepared by the hydrosilylation of alpha-omega alkenyl-terminated polyethers and dimethylhydrogen-terminated siloxane of varying degrees of polymerization (designated as $M'D_xM'$), in the presence of a platinum catalyst.

Materials

[0048] The representative $(AB)_n$ SPEs, used in the compositions of the present invention were prepared using the following starting materials.

M'D_xM' siloxanes – a series of dimethyl-hydrogen terminated (Me_2HSiO) linear polydimethylsiloxanes of varying degree of polymerizations (as designated by x) were prepared using well known siloxane polymerization techniques. The average formulas for this series of siloxanes are summarized in Table 1.

Allyl terminated polyethers – a series of alpha, omega-diallyloxy polyethers having the average formula $(CH_2=CHCH_2O(CH_2CH_2O)_mCH_2CH=CH_2)$ were used to prepare the $(AB)_n$ silicone polyether block copolymers.

Polyglycol AA600, AA1200, and AA2000, used as obtained from Clariant (Mt. Holly, NC), contained on average 12, 25, and 44 ethylene oxide units (designated as EO) (ie. $m = 12, 25,$ and 44)

Example 1*Preparation of a $(AB)_n$ SPE from a $M'D_{50}M'$ siloxane and AA1200 polyether*

[0049] A 1000 ml three neck round bottom flash equipped with temperature probe, electrical stirrer, and condenser was charged with 100.6 gram of Polyglycol AA1200 polyethylene glycol diallyl ether (Clariant Corp., Mt. Holly, NC), 61 gram of xylene and 0.28 gram of sodium acetate. The flask was heated to 100 °C. About 394.3 gram of dimethylhydrogen endblocked polydimethyl siloxane with a number average degree of polymerization of 50 DP was added dropwise via the addition funnel. After about 5 gram of the siloxane is added, about 0.60 gram of platinum catalyst (1,3-diethenyl-1,1,3,3-tetramethyldisiloxane platinum complex in dimethyl siloxane) was added to the mixture. When half of the siloxane was added, an additional 0.69 gram of Pt catalyst was added, followed by 0.71 gram of Pt when all the siloxane addition was complete. The reaction mixture was allowed to mix for about 1 hour for the polymer to grow. The xylene solvent was then removed via vacuum stripping at 150 °C. The weight-averaged molecular weight M_w of the silicone polyether copolymer was about 39,831 g/mole and polydispersity of 2.03.

Example 2*Preparation of a $(AB)_n$ SPE from a $M'D_{30}M'$ siloxane and AA1200 polyether*

[0050] A 2000 ml three neck round bottom flash equipped with temperature probe, electrical stirrer, and condenser was charged with 187 gram of Polyglycol AA1200 polyethylene glycol diallyl ether (Clariant Corp., Mt. Holly, NC), 52 gram of xylene and 0.25 gram of sodium acetate. The flask was heated to 100°C. About 329.76 gram of dimethylhydrogen endblocked polydimethyl siloxane with a number average degree polymerization of 30 DP (SiH @ 1050 ppm) was added dropwise via an addition funnel. After about 5 gram of the siloxane is added, about 0.57 gram of platinum catalyst (1,3-diethenyl-1,1,3,3-tetramethyldisiloxane platinum complex in dimethyl siloxane) was added to the mixture. When half of the siloxane was added, an additional 0.62 gram of Pt catalyst was added, followed by 0.8 gram of Pt when all the siloxane addition was complete. The reaction mixture was allowed to mixed for about 1 hour to allow for the polymer to grow. The xylene solvent was then removed via vacuum stripping at 150 °C. The weight-average molecular

weight Mw of the silicone polyether copolymer was about 35,171 g/mole and polydispersity of 2.01.

Example 3

5 *Preparation of a (AB)_n SPE from a M'D₇₅M' siloxane and AA1200 polyether*

[0051] A 2000 ml three neck round bottom flash equipped with temperature probe, electrical stirrer, and condenser was charged with 150 gram of Polyglycol AA1200 polyethylene glycol diallyl ether, 111 gram of xylene and 0.33 gram of sodium acetate. The flask was heated to 100 °C. About 329.76 gram of dimethylhydrogen endblocked polydimethyl siloxane with a number average degree polymerization of 75 DP (SiH @ 327.3 ppm) was added dropwise via an addition funnel. After about 5 gram of the siloxane was added, about 0.22 gram of platinum catalyst (1,3-diethenyl-1,1,3,3-tetramethyldisiloxane platinum complex in dimethyl siloxane) was added to the mixture. When half of the siloxane was added, an additional 0.42 gram of Pt catalyst was added followed by 0.37 gram of Pt when all the siloxane addition was complete. The reaction mixture was allowed to mixed for about 1 hour to allow for the polymer to grow. The xylene solvent was then removed via vacuum stripping at 150 °C. The weight-average molecular weight Mw of the silicone polyether copolymer was about 40,158 g/mole and polydispersity of 1.98.

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Example 4

Preparation of a (AB)_n SPE from a M'D₁₅M' siloxane and AA1200 polyether

[0052] A 2000 ml three neck round bottom flash equipped with temperature probe, electrical stirrer, and condenser was charged with 453 gram of Polyglycol AA1200 polyethylene glycol diallyl ether, 50 gram of xylene and 0.5 gram of sodium acetate. The flask was heated to 100°C. About 443 gram of dimethylhydrogen endblocked polydimethyl siloxane with a number average degree polymerization of 15 (SiH @ 1730 ppm) was added dropwise via an addition funnel. After about 5 gram of the siloxane was added, about 0.95 gram of platinum catalyst (1,3-diethenyl-1,1,3,3-tetramethyldisiloxane platinum complex in dimethyl siloxane) was added to the mixture. When half of the siloxane was added, an additional 0.74 gram of Pt catalyst was added, followed by 0.14 gram of Pt when all the siloxane addition was complete. The reaction mixture was allowed to mixed for about 1 hour to allow for the polymer to grow. The xylene solvent was then removed via vacuum stripping at 150 °C. The weight-

average molecular weight Mw of the silicone polyether copolymer was about 33,552 g/mole and polydispersity of 2.19.

Example 5

5 *Preparation of a (AB)_n SPE from a M'D₁₅M' siloxane and AA2000 polyether*

[0053] A 2000 ml three neck round bottom flash equipped with temperature probe, electrical stirrer, and condenser was charged with 601.6 gram of Polyglycol AA2000 polyethylene glycol diallyl ether (Clariant, Mt. Holly, NC), 54.9 gram of toluene. The flask was heated to 100°C. About 398.4 gram of dimethylhydrogen endblocked polydimethyl siloxane with a number average degree polymerization of 15 DP (SiH @ 1730 ppm) was added dropwise via an addition funnel. After about 5 gram of the siloxane was added, about 1.04 gram of platinum catalyst solution (1,3-diethenyl-1,1,3,3-tetramethyldisiloxane platinum complex in dimethyl siloxane) was added to the mixture. When half of the siloxane was added, an additional 1.95 gram of Pt catalyst solution was added, followed by 2.24 gram of Pt when all the siloxane addition was complete. The reaction mixture was allowed to mixed for about 1 hour to allow for the polymier to grow. The xylene solvent was then removed via vacuum stripping at 150 °C. The weight-averaged molecular weight Mw of the silicone polyether copolymer was about 44,247 g/mole and polydispersity of 1.77.

Example 6

25 *Preparation of a (AB)_n SPE from a M'D₅₀M' siloxane and AA1200 polyether (Vi / SiH molar ratio @ 1.1; made in xylene without sodium acetate)*

[0054] A 1000 ml three neck round bottom flash equipped with temperature probe, electrical stirrer, and condenser was charged with 105.8 gram of Polyglycol AA1200 polyethylene glycol diallyl ether, 100 gram of xylene.. The flask was heated to 100 °C. About 394.3 gram of dimethylhydrogen endblocked polydimethyl siloxane with a number average DP of 50 (SiH @ 498.4 ppm) was added dropwise via an addition funnel. After about 5 gram of the siloxane was added, about 0.60 gram of platinum catalyst (1,3-diethenyl-1,1,3,3-tetramethyldisiloxane platinum complex in dimethyl siloxane) was added to the mixture. When half of the siloxane was added, an additional 0.69 gram of Pt catalyst was added, followed by 0.71 gram of Pt when all the siloxane addition was complete. The reaction mixture was allowed to mixed for about 1 hour to allow for the polymer to grow. The xylene

solvent was then removed via vacuum stripping at 150 °C. The weight-average molecular weight Mw of the silicone polyether copolymer was about 50,108 g/mole and polydispersity of 2.12.

5 **Example 7**

Preparation of a (AB)_n SPE from a M'D₁₅M siloxane and AA2000 polyether

10 [0055] A 2000 ml three neck round bottom flash equipped with temperature probe, electrical stirrer, and condenser was charged with 150.4 gram of Polyglycol AA2000 polyethylene glycol diallyl ether, 50 gram of toluene. The flask was heated to 100°C. About 99.6 gram of dimethylhydrogen endblocked polydimethyl siloxane with a number average DP of 15 was added dropwise via an addition funnel. After about 5 gram of the siloxane was added, about 0.5 gram of platinum catalyst (1,3-diethenyl-1,1,3,3-tetramethyldisiloxane platinum complex in dimethyl siloxane) was added to the mixture. When half of the siloxane was added, an additional 0.5 gram of Pt catalyst was added followed by 0.2 gram of Pt when all the siloxane 15 addition was complete. The reaction mixture was allowed to mixed for about 1 hour to allow for the polymer to grow. The xylene solvent was then removed via vacuum stripping at 150 °C. The weight-average molecular weight Mw of the silicone polyether copolymer was about 22,248 g/mole and polydispersity of 1.4.

[0056] The $(AB)_n$ SPEs of Examples 1 – 7 were evaluated for their ability to form vesicles or stable dispersions upon mixing with water. The results of which are summarized in Table 1.

5

Table 1

Example #	Siloxane block DP	Polyether block	Aqueous mixing behavior
1	M'D ₅₀ M'	EO ₁₂	vesicles
2	M'D ₃₀ M'	EO ₁₂	vesicles
3	M'D ₇₅ M'	EO ₁₂	vesicles
4	M'D ₁₅ M'	EO ₁₂	stable dispersion
5	M'D ₁₅ M'	EO ₂₂	stable dispersion
6	M'D ₅₀ M'	EO ₁₂	vesicles
7	M'D ₁₅ M'	EO ₂₂	stable dispersion

Example 8

Preparation of a (AB)_n SPE from a M'D₅₀M' siloxane and AA1200 polyether

- 5 [0057] A 2000 ml three neck round bottom flash equipped with temperature probe, electrical stirrer, and condenser was charged with 153 gram of Polyglycol AA1200 polyethylene glycol diallyl ether, .4 gram of sodium acetate, 83.7 gram of isopropanol alcohol. The flask was heated to 85°C. About 647 gram of dimethylhydrogen endblocked polydimethylsiloxane with a number average DP of 50 was added dropwise via an addition funnel over a period of
10 about 25 minutes. After about 5 gram of the siloxane was added, about 0.56 gram of platinum catalyst (1,3-diethenyl-1,1,3,3-tetramethyldisiloxane platinum complex in dimethyl siloxane) was added to the mixture. When half of the siloxane was added, an additional 0.45 gram of Pt catalyst was added, followed by 0.46 gram of Pt when all the siloxane addition was complete. The reaction mixture was allowed to mixed for about 1 hour to allow for the
15 polymer to grow. The IPA solvent was then removed via vacuum stripping at 100 °C. The weight-averaged molecular weight Mw of the silicone polyether copolymer was about 44,375 g/mole and polydispersity of 2.14.

20 **Examples 9 & 10**

- [0058] A similar procedure to Example 8 was followed to prepare two other (AB)_n SPEs, labeled as Example 9 and Example 10. The only variation was the amount of Polyglycol AA1200 polyether used, as shown in the Table 2, to demonstrate the preparation of (AB)_n
25 SPEs from a process where the vinyl/SiH ratio ranged from 1/1 to 1.75/1.

Example 11

Preparation of a (AB)_n SPE from a M'D₅₀M' siloxane and AA1200 polyether - by one-step process in IPA

- 30 [0059] A 3000 ml three neck round bottom flash equipped with temperature probe, electrical stirrer, and condenser was charged with 199 gram of Polyglycol AA1200 polyethylene glycol diallyl ether, .4 gram of sodium acetate, 84.5 gram of isopropanol alcohol. Also added to the flask was about 647 gram of dimethylhydrogen endblocked polydimethyl siloxane with a
35 number average DP of 50. The flask was heated to 85°C. Half of the Pt was added, about

0.76 gram, to initiate the reaction. About 10 minutes later, the remaining Pt was added. The reaction mixture was allowed to mixed for about 1 hour to allow for the polymer to grow. The IPA solvent was then removed via vacuum stripping at 100 °C. The weight-average molecular weight M_w of the final silicone polyether copolymer was about 48,034 and polydispersity of 2.10. ^{29}Si NMR analysis showed no detectable Si-O-C bond formation, indicative of a clean hydrosilylation reaction. This example illustrates that $(\text{AB})_n$ SPEs of same or higher molecular weight and purity can be produced from a homogeneous mixture of siloxane and polyether at stoichiometric or slightly higher ratio.

Table 2

Example #	8	9	10	11
Polyglycol AA1200, g	153.0	199.2	267.22	199.2
50 dp siloxane, g	647.0	647.0	647.0	647.0
Vi / SiH molar ratio	1.0	1.3	1.75	1.3
Siloxane addition method	Slow addition	Slow addition	Slow addition	Added altogether before catalyzed
Solvent type	IPA	IPA	IPA	IPA
Pt catalyst, g	1.47	1.47	1.62	1.52
M_w , g/mole	44,375	43,105	35,857	48,034
Polydispersity	2.14	2.13	2.16	2.10
% Polymer peak	96.8	96.5	85.5	96.9
% Low mw peak	3.2	3.5	14.5	3.1

Examples 12 & 13

Vesicle Compositions containing Vitamin A Palmitate from the $(\text{AB})_n$ SPEs of Examples 9 & 11

[0060] The following procedure was used to prepare the vesicle compositions summarized in Table 3 as Examples 12 and 13.

[0061] Ethanol (EtOH) was added to $(\text{AB})_n$ SPE of Example 9, a $(\text{AB})_n$ block copolymer of $\text{M}'\text{D}_{50}\text{M}'$ siloxane and polyglycol AA1200 polyether, having a weight-average molecular weight M_w of 43,105 g/mole), to provide a homogeneous mixture. With continuous mixing, water was added slowly to form a homogeneous dispersion. The mixture was subsequently homogenized to a mixture having an average particle size of 0.214 μm . The EtOH in the

dispersion was then removed using a Rotovapor under vacuum at ambient temperature, to yield an alcohol-free, homogeneous dispersion having an average particle size of 0.359 μm , designated as Example 12.

[0062] A vesicle composition using $(\text{AB})_n$ SPE of Example 9 was also made following the same procedure and summarized as Example 13.

[0063] The final compositions for these two vesicle dispersions are summarized in Table 3. Removal of the volatile alcohol (EtOH) did not compromise the quality of the dispersion.

[0064] These dispersions were also examined under a polarized light and were shown to be anisotropically light reflective. This is indicative of the presence of vesicular structure in

these dispersions. The vesicle sizes and particle size distributions are shown in the Table 3.

Table 3

Example #	12	13
(AB)n SPE reference	Example 9	Example 11
(AB)n SPE, g	58.48	59.25
Vitamin A Palmitate mixture, g	17.83	18.11
EtOH, g	84.38	85.42
Water, g	205.93	208.38
Batch size, before strip	366.61	371.16
Amount Removed	92.50	86.10
Final batch size, g	274.11	274.11
<i>Vesicle dispersion composition</i>		
% (AB)n SPE Polymer	21.33	21.07
% VAP	4.65	4.53
% 1-2287 silicone fluid	1.16	1.13
% stabilizers	0.69	0.68
% Water	72.16	72.58
Appearance	Smooth yellow dispersion	Smooth yellow dispersion
pH of vesicle dispersion	6.00	6.23
Average vesicle size Mv, μm	0.359	0.806
Size @ 50%, μm	0.342	0.77
Size @ 90%, μm	0.554	1.586

CLAIMS

1. A polyorganosiloxane-polyoxyethylene block copolymer having the average formula;



where x and y are greater than 4, and $x/(x+y)$ ranges from 0.2 to 0.9,

z is greater than 2,

R is independently a monovalent organic group, and

R^1 is a divalent organic group containing 1 to 12 carbons.

2. The polyorganosiloxane-polyoxyethylene block copolymer of claim 1 wherein x has a value ranging from 20 to 100.

3. The polyorganosiloxane-polyoxyethylene block copolymer of claim 1 wherein x has a value ranging from 5 to 19.

4. The polyorganosiloxane-polyoxyethylene block copolymer of claims 1, 2, or 3 wherein R is methyl and R^1 is propylene.

5. A process to prepare a polyorganosiloxane-polyoxyethylene block copolymer comprising reacting;

a) a SiH terminated organopolysiloxane,

b) a polyoxyethylene having an unsaturated organic group at each molecular terminal,

c) a hydrosilylation catalyst,

d) optionally a solvent,

e) optionally an organic endblocker compound having a mono-terminally unsaturated organic group,

wherein the mole ratio of the unsaturated organic groups to SiH in the reaction is at least 1:1.

6. The process of claim 5 wherein the SiH terminated organopolysiloxane has the average formula $\text{Me}_2\text{HSiO}(\text{Me}_2\text{SiO})_x\text{SiHMe}_2$ and x is greater than 4.

7. The process of claim 5 wherein the polyoxyethylene has the average formula

5 $\text{H}_2\text{C}=\text{CHCH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_y\text{CH}_2\text{CH}=\text{CH}_2$ wherein y is greater than 4.

8. The product made by the process of claims 5, 6, or 7.

9. A vesicle composition comprising the product of claim 8.

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10. An aqueous dispersion comprising the product of claim 8.

INTERNATIONAL SEARCH REPORT

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A. CLASSIFICATION OF SUBJECT MATTER
 IPC 7 C08G77/46 C08L83/12

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4 150 048 A (SCHILLING, JR. ET AL) 17 April 1979 (1979-04-17) claims 1-10; examples 15-17	1-10
X	US 5 472 686 A (TSUBAKI ET AL) 5 December 1995 (1995-12-05) claim 8; examples 3-6	1-10
X	EP 0 896 015 A (WITCO CORPORATION; GENERAL ELECTRIC COMPANY) 10 February 1999 (1999-02-10) page 5, line 7 - page 7, line 10; examples 1-3,5	1-8
A	US 5 411 744 A (HILL ET AL) 2 May 1995 (1995-05-02) the whole document	1-10

☐ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

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Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 4150048	A	17-04-1979	NONE	
US 5472686	A	05-12-1995	JP 3071222 B2	31-07-2000
			JP 4234307 A	24-08-1992
			AT 133558 T	15-02-1996
			CA 2058461 A1	29-06-1992
			DE 69116839 D1	14-03-1996
			EP 0492657 A1	01-07-1992
			JP 3061434 B2	10-07-2000
			JP 4211605 A	03-08-1992
			US 5660819 A	26-08-1997
			DE 69116839 T2	04-07-1996
			KR 158212 B1	01-12-1998
EP 0896015	A	10-02-1999	US 5869727 A	09-02-1999
			BR 9815761 A	26-12-2000
			CA 2242303 A1	08-02-1999
			CN 1208741 A	24-02-1999
			DE 69827083 D1	25-11-2004
			DE 69827083 T2	03-03-2005
			EP 0896015 A1	10-02-1999
			JP 11116670 A	27-04-1999
US 5411744	A	02-05-1995	US 5364633 A	15-11-1994
			DE 69509574 D1	17-06-1999
			DE 69509574 T2	07-10-1999
			EP 0672410 A1	20-09-1995
			JP 7323222 A	12-12-1995

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